FIELD EMISSION GUN SCANNING ELECTRON (FEGSEM) AND TRANSMISSION ELECTRON (TEM) MICROSCOPY OF PHYLLOSILICATES IN MARTIAN METEORITES ALH84001, NAKHLA, AND SHERGOTTY; Kathie L. Thomas-Keprta[1], Susan J. Wentworth[1], David S. McKay[2], and Everett K. Gibson[3]; [1]Lockheed Martin, Mail Code C-23, NASA/JSC, Houston, Tx, 77058, [2]NASA/JSC, SN, Houston, TX 77058, [4]NASA/JSC, SN4, Houston, TX 77058

Martian meteorites ALH84001, Nakhla, and Shergotty have a wide span of igneous ages ranging from ~4.5 Ga to 1.3 Ga to 165 Ma, respectively [e.g., 1] and thus represent historical snapshots of Mars. We have examined these three martian meteorites for the presence of layer lattice silicates (LLS) or phyllosilicates using FEGSEM and TEM. Here we document the occurrence of phyllosilicates and alteration phases in these meteorites, suggest formation conditions required for phyllosilicate formation and speculate on the extent of fluid:rock interactions during the past history of Mars.

Methods Chips from ALH84001, Nakhla, and Shergotty were prepared for FEGSEM [technique described in 2]. Samples of ALH84001 and clay-containing veins in Nakhla were prepared for TEM [technique described in 3]. Energy dispersive spectroscopy (EDS) analyses were performed on samples examined by both FEGSEM and TEM.

ALH84001 Carbonates, in the form of pancake-shaped globules, have been described from Martian meteorite ALH84001 and are proposed to have precipitated from low temperature brine solutions on Mars [e.g. 4, 5]. Thus it is likely that some evidence for hydrated minerals should exist in this orthopyroxene-rich meteorite. Previous studies by various workers have suggested that clays are not evident; however, Brearly [6] reported a K-bearing mica within a carbonate fragment embedded in feldspathic glass, and other minor occurrences have been reported previously [7]. Our further detailed SEM and TEM analyses show that hydrated minerals are present at carbonate-pyroxene boundaries (Fig. 1) and also on pyroxene surfaces not in contact with carbonate (Fig. 2). Individual packets (nm-sized) and relatively large regions (~500 nm in size) of phyllosilicates are present. It appears that ALH84001 phyllosilicates are distributed in small, scattered regions and, therefore, their total volume percent within the meteorite may be underestimated. The basal spacings measure 1.0-1.1 nm suggesting this is a smectite-type clay. Compositions of phyllosilicates in ALH84001 have not been reported previously. These smectite-like clays are composed mainly of Si, Mg, and O with minor Fe (10-15 oxide percent) and Al (ranging from 2.5-3.5 oxide percent). Textural and compositional observations support smectite formation on Mars, not Earth.

Nakhla Phyllosilicates are common in vein filling material. These vein fillings previously described as iddingsite [e.g., 8] (an alteration product of olivine) are composed of smectitic phyllosilicates, nanometer-sized iron oxides, and crystalline silica phases including quartz, cristobalite, tridymite, and a Si-rich amorphous phase. Previous reports of iddingsite have shown that a mixture of phyllosilicates is present [8] but we found only phyllosilicates with 1 nm spacings having compositions similar to ALH84001 smectite (Fig. 3). Fe-oxides are found in discrete clumps composed of hematite and goethite; anhedral particles < 30 nm are typically hematite while larger euhedral grains are composed of hematite, goethite, or a mixture of both (some of the larger Fe- oxides appear to be aggregates of smaller particles of hematite and goethite). Most of the Fe oxides are embedded in amorphous silica or smectite (Fig. 4). Most Fe oxides appear to be chemically pure, although some have detectable Cr. Crystalline and amorphous silica are also present both as large (500 nm grains) and small (<100 nm) grains. It appears that some of the amorphous silica is initially crystalline and rapidly becomes amorphous within seconds due to interaction with the electron beam Typically the amorphous silica phase is composed only of Si and O.

Shergotty Our preliminary FEGSEM analyses show the presence of phyllosilicates (Fig. 5). Other secondary weathering minerals are present including NaCl, Ca-sulfate, and possibly Mg-chloride [2]. Similar salts have been detected in Nakhla [8] and provide further evidence for hydrous alteration in both meteorites. Textural relationships suggest that some, if not all, of these secondary minerals formed on Mars, not Earth [2,8].

Formation Conditions The presence of phyllosilcates in ALH84001, Nakhla and Shergotty indicates that liquid water was present on Mars. It is likely that an aqueous phase interacted with each of these Martian samples at some time during their residence on Mars. Our results suggest that the fluids that interacted with each of these meteorites had different properties. For example it appears that fluids that interacted with Nakhla were much more oxidizing (e.g., Fe^{+3} in goethite and hematite) than those for ALH84001 (e.g., Fe^{+2} and Fe^{+3} in magnetite). The compositions of the carbonates have also been used to characterize the fluids from which they precipitated. Extensive laboratory work has shown that carbonates with similar zoning patterns to those in ALH84001 can be produced at pH 6-7, with high CO_2 partial pressure, using Mg-rich supersaturated solutions containing Ca, Mg, Fe ions at 150°C [9]; however, phyllosilicates were not produced using these experimental conditions. Figure 1 shows that the ALH84001 phyllosilcates can be intimately associated with both the carbonate globules and the pyroxene, suggesting different formation conditions (e.g., lower CO_2 partial pressures) than suggested by [9]. Other workers, including [10], suggested that the fluid phase in ALH84001 may have been basic with pH>7. In addition to this work, phyllosilicates have been reported in other martian meteorites (e.g., Lafayette [11], Gov. Valadares [12]). The presence of phyllosilicates and salts in martian meteorites of widely different formation ages is strong evidence that aqueous phases on or beneath the surface of Mars were likely present over much of martian history. Additional data on martian secondary vein filling material may provide important new constraints on the aqueous history of Mars.

References: [1] McSween H.Y. (1994) *Meteoritics* **29**, 757.[2] Wentworth S.J. *et al*. This volume [3]Thomas K.L. *et al*. (1993) *GCA* **57**, 1551. [4] Warren P.H. (1998) *JGR* **103**, 16759. [5] McSween H.P. and Harvey R. (1998*) Internat.Geol. Rev*. **40**, 774. [6] Brearley A. J. (1998) LPI Contribution #956, 6. [7] Wentworth S.J. *et al*. (1998) *LPSC* **XXIX**, abst # 1793. [8] Gooding J.L. *et al.* (1991) *Meteoritics* **26**, 135. [9] Golden D.C. *et al*. (2000) *Met.& Planet. Sci.* (in press). [10] Wentworth S.J. and Gooding J.L.(1995) *LPSC* **XXVI**, 1489-1490. [11] Treiman A.H. *et al.* (1993) *Meteoritics* **28**, 86. [12]

Figure 1. Smectite surrounding ALH84001 carbonate grains in the interior/rim of a carbonate globule. The phyllosilicates extend from the surrounding OPX into the carbonate. Bottom image is an enlarged view of the boxed area.

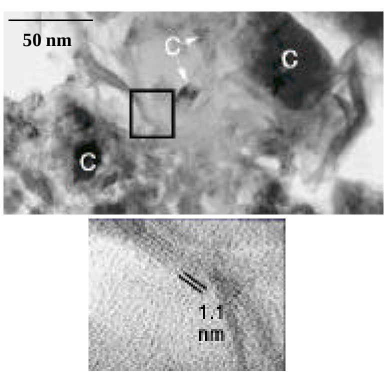

Figure 2. FEGSEM image of uncoated (left) and c-coated (right) phyllosilicates on OPX in ALH84001.

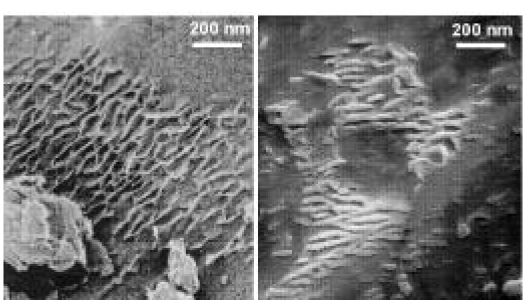

Figure 3. Smectite in vein filling material from Nakhla. Top image is a high magnification view of region in box in the lower image showing 1 nm spacings for smectite. The lower view shows a low magnification view of amorphous silica (smooth region in the upper left corner) and smectite (curly-looking material).

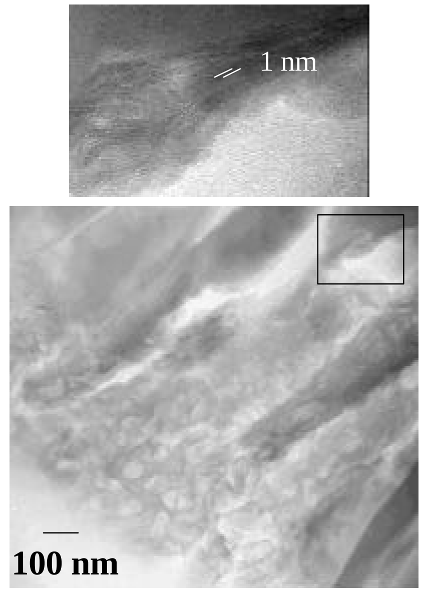

Figure 4. Fe-oxide grain in Nakhla. Smaller hematite crystal (right) is ~30 nm. (LLS is layer lattice silicate).

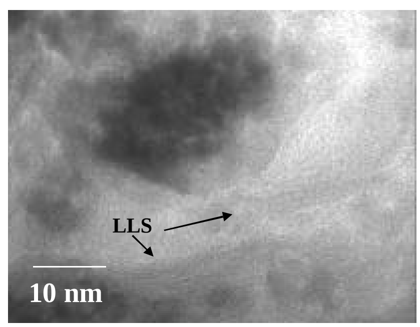

Figure 5. FEGSEM images of phyllosilicates on pyroxene surfaces of Shergotty . This texture is typical of many types of smectite-like phyllosilicates.